



Short communication

## Intrinsically microporous polymer slows down fuel cell catalyst corrosion



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### ABSTRACT

The limited stability of fuel cell cathode catalysts causes a significant loss of operational cell voltage with commercial Pt-based catalysts, which hinders the wider commercialization of fuel cell technologies. We demonstrate beneficial effects of a highly rigid and porous polymer of intrinsic microporosity (PIM-EA-TB with BET surface area 1027 m<sup>2</sup> g<sup>-1</sup>) in accelerated catalyst corrosion experiments. Porous films of PIM-EA-TB offer an effective protective matrix for the prevention of Pt/C catalyst corrosion without impeding flux of reagents. The results of electrochemical cycling tests show that the PIM-EA-TB protected Pt/C (denoted here as PIM@Pt/C) exhibit a significantly enhanced durability as compared to a conventional Pt/C catalyst.

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## 1. Introduction

Polymer electrolyte fuel cells have been extensively investigated as ideal energy sources for portable electronic devices and for electric vehicles due to their high power density and use of environmentally friendly fuels [1–3]. However, the expensive metal catalyst Pt, supported on carbon black (here using as the most common electrocatalyst (Pt/C) with 40% Pt on Vulcan 72 [4]) during operation suffers from Pt dissolution [5], Ostwald ripening [6], nanoparticle mobility and aggregation [7], and carbon support electrochemical corrosion [8] in the harsh working environment within polymer electrolyte fuel cells. This commonly leads to a rapid and significant loss of electrochemical surface area [9] (ECA). This drawback, and the problem of slow kinetics of oxygen reduction reaction (ORR) at fuel cell cathodes, still severely hamper the commercialization of fuel cell technology [10,11].

Porous materials such as zirconia [12], silica [13], or tin oxide [14] were supposed to inhibit the migration of metal nanoparticles on catalyst supports. The porous support structure is an attractive way to enhance the stability of metal nanoparticles without affecting the transport of reactants and products. However, with inorganic materials, there is still a challenge in precisely controlling the thickness of porous overlayers and avoiding decrease in catalytic activity. Recently, a novel class of microporous organic materials, polymers with intrinsic microporosity (PIM), has been developed. There are a range of potential

applications in gas membrane technology [15,16], in electrolyte media as ionic diode [17], and in electrochemical technology [18,19]. The structurally highly rigid PIM backbone achieves open packing to generate novel properties due to permanent microporosity with ion permeability or semipermeability.

In this study, we exploit a highly porous polymer of intrinsic microporosity (PIM-EA-TB with BET surface area 1027 m<sup>2</sup> g<sup>-1</sup>) as a protection agent for commercial fuel cell catalyst (Pt/C catalyst with 40% Pt on Vulcan-72). Fig. 1 schematically shows PIM-EA-TB acting as a stabilizer for the Pt/C catalyst particles.

## 2. Experimental

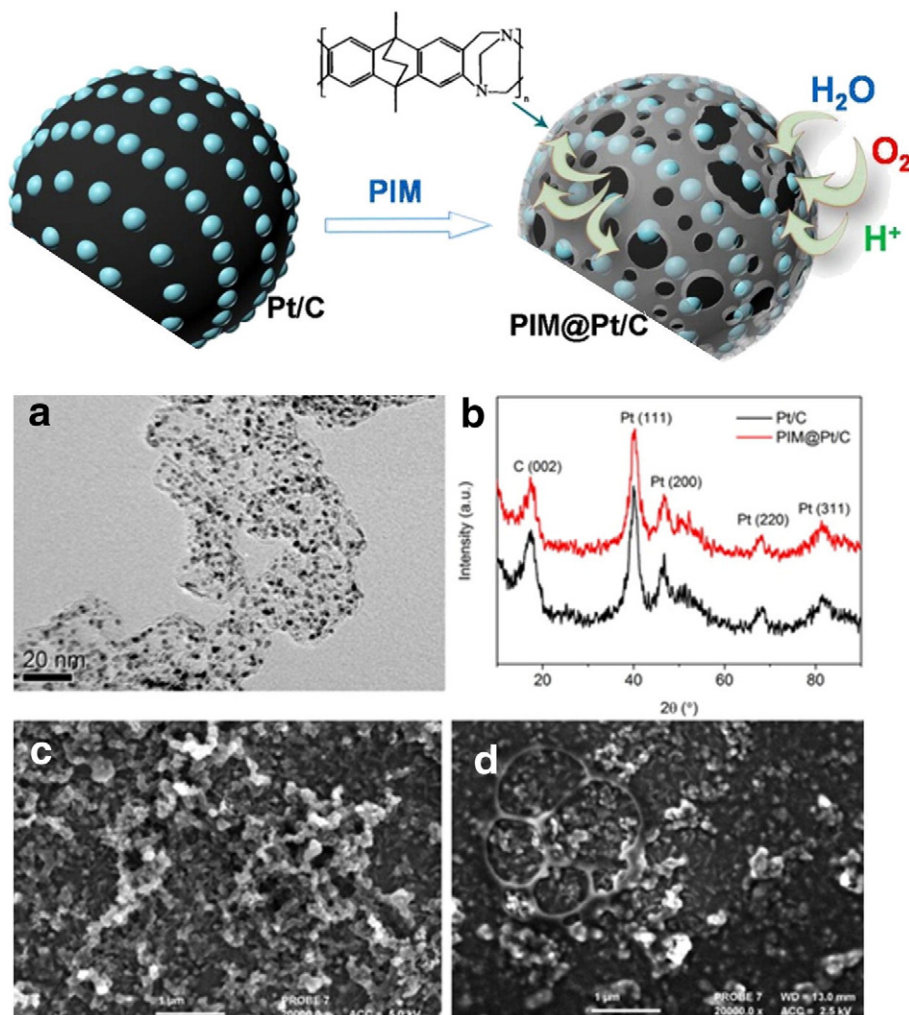
### 2.1. Chemical reagents

Commercial Pt/C (40 wt. % on Vulcan-72) catalyst and Nafion (5 wt. %) were obtained from Johnson–Matthey and Sigma–Aldrich, respectively. Isopropanol, chloroform, and perchloric acid (70%–72%), were purchased from Aldrich. PIM-EA-TB was prepared following a literature recipe [20]. Solutions were prepared with filtered and deionized water of resistivity 18.2 MΩ cm from a Thermo Scientific water purification system (ELGA).

### 2.2. Instrumentation

Electrochemical measurements were performed with a μAutolab III system in a conventional three electrode cell with KCl-saturated

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**Fig. 1.** Schematic illustration of Pt/C catalyst protection by PIM-EA-TB. (a) TEM image of Pt/C catalyst. (b) XRD patterns of Pt/C and PIM@Pt/C. SEM images of (c) Pt/C and (d) PIM@Pt/C on glassy carbon electrodes.

calomel (SCE) reference (which is 0.241 V vs. NHE) and platinum wire counter. A Pine AFMSRCE electrode rotator was used for rotating disk electrode (RDE) experiments. Morphologies of the prepared catalysts were analyzed with a JEOL FESEM6301F scanning electron microscope (SEM) and a JEOL 2010 high-resolution transmission electron microscope (HRTEM). TEM samples before and after accelerated degradation testing were prepared by ultrasonically dispersing catalyst from the glassy carbon electrode surface into 2 cm<sup>3</sup> ethanol. A volume of 5  $\mu$ L of the resulting dispersion was deposited onto an amorphous carbon/Cu grid. XRD spectra were obtained on X-ray diffraction (XRD Bruker D8 ADVANCE, Madison, WI, USA) with a mono-chromatized source of Cu-K $\alpha$  radiation.

### 2.3. Procedures for electrode preparation

2 mg of Pt/C catalyst and 100  $\mu$ L of 5 wt. % Nafion solution were dispersed in 1 mL of isopropanol, followed by a sonication for 15 min to form a homogeneous catalyst ink. 8  $\mu$ L of the ink was loaded onto a glassy carbon (GC) disk electrode with a diameter of 6 mm. The catalyst layer was allowed to dry under ambient conditions before electrochemical measurement. Coatings with PIM-EA-TB on Pt/C to give PIM@Pt/C were applied as follows: a solution of 1 mg mL<sup>-1</sup> PIM-EA-TB (10  $\mu$ L) in chloroform was applied directly onto the Pt/C catalyst layer followed by drying under ambient conditions.

## 3. Results and discussion

### 3.1. Physical characterization

Fig. 1a shows TEM images of Pt/C catalyst with a size range of 3–5 nm for Pt nanoparticles supported on carbon black. The XRD patterns of Pt/C and PIM@Pt/C are shown in Fig. 1b. The peaks between 20° and 90° are indexed to Pt crystals of face-centered cubic (fcc) structure. The peaks at  $2\theta = 39.70^\circ$ ,  $46.46^\circ$ ,  $67.70^\circ$ , and  $81.42^\circ$  are assigned to the (111), (200), (220), and (311) planes of Pt, respectively. The presence of PIM did not affect the Pt/C catalyst. Fig. 1c,d show SEM images of Pt/C and PIM@Pt/C catalysts on glassy carbon electrode surfaces. It can be seen that a PIM-EA-TB membrane layer is distributed over the catalyst layer surface.

### 3.2. Electrochemical characterization of activity and durability

Fig. 2a shows cyclic voltammetry data for the Pt/C and for PIM@Pt/C catalysts recorded in de-aerated 0.1 M HClO<sub>4</sub> at room temperature. The electrochemical surface area (ECA) was calculated from the charge under the hydrogen adsorption/desorption region with double-layer charging correction and assuming a value of 210  $\mu$ C cm<sup>-2</sup> for the adsorption of a hydrogen monolayer [21]. The PIM@Pt/C catalyst exhibits a very similar electrochemically active surface area (52.6 m<sup>2</sup> g<sup>-1</sup>) compared to Pt/C (53.7 m<sup>2</sup> g<sup>-1</sup>). Very similar polarization curves for

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